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SYNTHESIS AND THERMAL CURING PARAMETERS OF A NOVEL PHENYLQUINOXALINE CONTAINING BOTH TERMINAL ETHYNYL AND PENDANT PHENYLETHYNYL GROUPS

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Nonmetallic Materials Division

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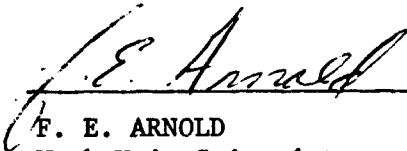WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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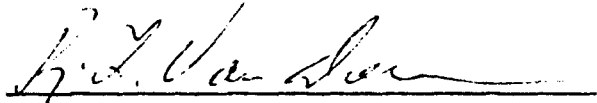Work Unit Scientist

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The synthesis of 3,3'-bis(4-[3-ethynylphenoxy]phenyl)-7,7'-bis(phenyl-ethynyl)-2,2'-diphenyl-6,6'-biquinoxaline (I) was accomplished by reaction of 2,2'-bis(phenylethynyl)-5,5'-diaminobenzidine (II) and 4-(3-ethynylphenoxy) benzil. Thermal analysis of I indicated a softening temperature of 107°C, followed by an exotherm above 150°C corresponding to independent crosslinking reaction of the terminal acetylene groups and intramolecular cycloaddition (IMC) reaction of the 2,2'-bis(phenylethynyl)biphenyl moieties. In the course

20. ABSTRACT (Cont'd)

of the synthetic work, substantial improvements were made in the synthesis of II.

The sample of I was cured at 200°C and the maximum partially cured transition temperature attained was 280°C. A sample of 3,3'-bis(4-[3-ethynyl-phenoxy]phenyl)-2,2'-diphenyl-6,6'-biquinoxaline was similarly tested as a model without IMC capability, and its corresponding value was 250°C. The difference in these two values is briefly discussed.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. This work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFWAL/ML Work Unit Scientist. This report describes work conducted from April 1977 to January 1980.

The work described in this report was conducted in the Polymer Branch Laboratory by Dr. F. L. Hedberg, Dr. C. Y-C. Lee and Dr. I. J. Goldfarb of the Materials Laboratory. The manuscript was released by the authors in June 1980 for publication as a Technical Report.

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SECTION I

INTRODUCTION

A novel method of curing aromatic-heterocyclic polymer systems by means of nonvolatile intramolecular cycloaddition (IMC) reactions along the polymer backbone has been reported (References 1 and 2) to afford highly rigid, thermooxidatively stable polymers with Tg's far in excess of the cure temperature used. The IMC reaction utilized for these quinoxaline and imide polymers (Equations 1 and 2) was the established (References 3 and 4) thermal conversion of 2,2'-bis(phenylethynyl)biphenyl to 9-phenyldibenz-[a,c]-anthracene.

A major drawback to processing the polymers was their high initial Tg and bulk viscosity which did not allow adequate softening to take place before the cure onset. A possible solution to this problem was suggested by recent work on quinoxaline oligomers with low softening temperatures which undergo a thermosetting polymerization through inter-molecular reaction of terminal acetylene groups (References 2, 5, and 6). This technical report describes the results of combining pendant pheny-lethynyl IMC reactions and terminal ethynyl thermoset reactions in the same molecule.

SECTION II

RESULTS AND DISCUSSION-SYNTHESIS

The system chosen for study was 3,3'-bis(4-[ethynylphenoxy]phenyl-7, 7'-bis(phenylethynyl)-2,2'-diphenyl-6,6'-biquinoxaline(II) which was prepared by the reaction of 2,2'-bis(phenylethynyl)-5,5'-diaminobenzidine(I) with 4-(3-ethynylphenoxy)benzil.

I

3)

II
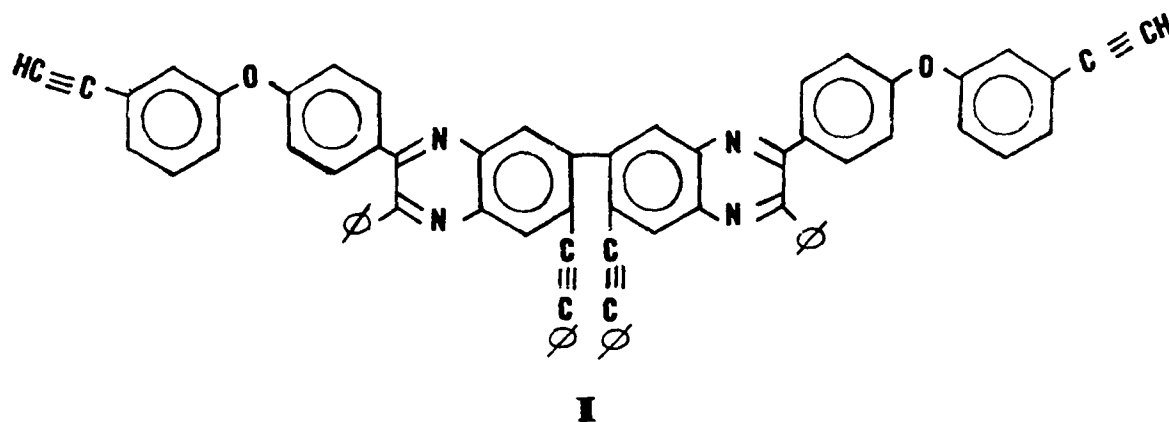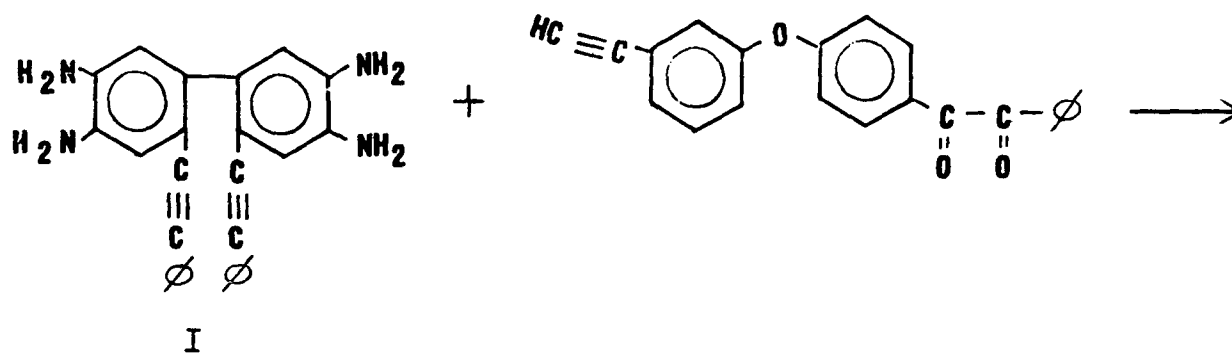
In the course of the preparative work, the reported (Reference 1)
7-step synthesis of I was improved substantially by modifications in the
first three steps. The use of an ethanol-ethylene glycol solvent for the
conversion of 3-iodonitrobenzene to 3,3'-diiodoazoxybenzene resulted in
a modest increase in yield for this reaction. The benzidine rearrangement
of 3,3'-diiodoazoxy-benzene to 2,2'-diiodobenzidine was modified and
combined with subsequent acylation to N,N'-diacetyl-2,2'-diiodobenzidine
to bypass isolation of 2,2'-diiodobenzidine. These changes resulted in
an increase in overall yield for the first three steps in the preparation
of I from 13% to 45%. Attempts were also made at varying conditions for
the sixth step of the synthesis in which 2,2'-diiodo-5,5'-dinitrobenzidine
was reacted with copper phenylacetylide to afford 2,2'-bis(phenylethynyl)-
5,5'-dinitrobenzidine(III).

Yields from this reaction
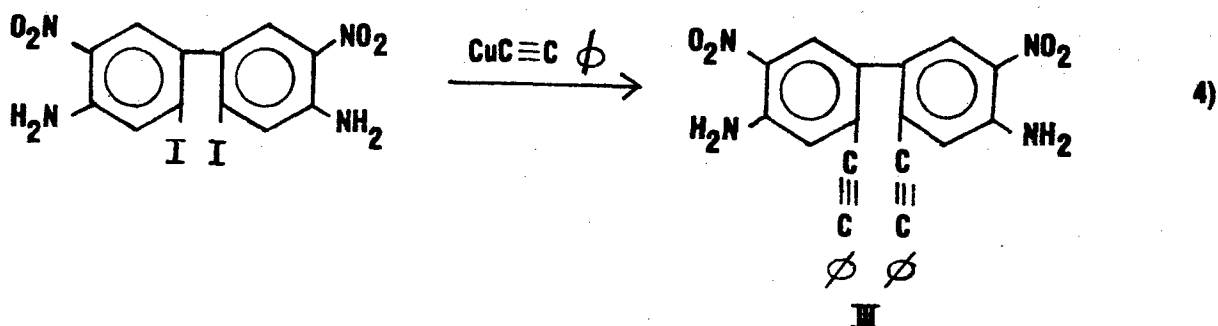
have ranged in our hands from 42-57%. Two recently reported procedures
for replacing iodine in iodoaromatics with phenylacetylene utilized either
a bis-(triphenylphosphine) palladium dichloride-cuprous iodide catalyst
in diethylamine (Reference 6) or a triphenyl phosphine-palladium acetate
catalyst in triethylamine (Reference 7). The former procedure afforded
yields of III of up to 31%, while the latter method resulted only in
decomposition of the starting material. It is possible that the steric
limitations imposed by the 2,2'-diiodobiphenyl moiety prevent formation
of the proposed (References 6 and 7) intermediate organopalladium complex.

The softening temperature for II, by analogy with the corresponding
3,3'-bis(4-[3-ethynylphenoxy]phenyl)-2,2'-diphenyl-6,6'-biquinoxaline(IV)
molecule with hydrogens in place of the pendant phenylethynyl groups
(Reference 8) was expected to be in the vicinity of 100°C. It was then
expected that at a temperature somewhere above 150°C both types of
acetylene groups in II would start to react.

DSC analysis was carried out on II to reveal an endothermic transition
corresponding to a softening temperature of 170°C. An exothermic tran-
sition was seen to begin 150°C with a maximum at 225°C. This temperature
range corresponds to the range found for the reaction exotherm of both the
terminal acetylenes and the 2,2'-bis(phenylethynyl) biphenyl system.

SECTION III

RESULTS AND DISCUSSION
THERMAL CURING PARAMETERS

IMC can be a useful modification on polymers in two ways: 1) it can lower the required processing temperature, or 2) it can increase the resultant Tg at a curing temperature. Polymers with rigid backbones usually have a higher Tg, but also require higher processing temperatures in composite or structural parts fabrication. Putting IMC sites into a polymer will soften the backbones, thus lowering the processing temperature. The IMC reaction can then be induced after processing to obtain its backbone rigidity and high Tg. This is not different from the thermoset concept, except that the cured polymer will not be highly crosslinked, thus may avoid some of the brittleness problems associated with highly crosslinked thermoset systems. The second possible advantage of IMC is that the reaction is not diffusion controlled. For most thermoset systems, curing will stop after vitrification because in the glassy state, long range chain motion is prohibited; only reactive groups in close proximity of each other can react. The resultant Tg of the cured product is then slightly above the cure temperature. If a higher Tg is desired, a higher curing temperature is needed. The upper Tg limit the system can attain is then the Tg (∞), the Tg associated with the system when all the reactive groups are reacted. This cure temperature and Tg relationship is shown in Figure 1. The dotted line denotes the Tcure = Tg curve. For most systems, the resultant Tg is above Tcure, so the cure vs Tg curve should lie above the dotted line. The advantage of an IMC system is then to have a cure vs Tg curve lie even further above the Tcure = Tg curve.

Denoting the Tg of the uncured resin as Tg(0), and the Tg of the completely cured system as Tg(∞), we call the Tg associated with an incompletely cured system as Tg(n) with 0 $<n<\infty$. To show that a system with IMC indeed has a higher Tcure vs Tg curve than a corresponding system without IMC, a comparison of their Tg(n)'s at identical curing temperature is needed. Previous experiments with epoxy (Reference 9) have shown that conventional thermal scan to detect Tg(n) may not be an appropriate method if the kinetic rate of curing is fast. The

experimentally observed transition $Tg(n_{ob})$ may not be the Tg associated with the state of interest, n_i, but of a more advancely cured state, i.e. $n_{ob} > n_i$. Sometimes if the kinetic rate is fast enough, the only transition that will be detected is $Tg(\infty)$ regardless of cure history.

This indeed is the case for the previously reported (Reference 8) 3,3'-bis(4-[3-ethynylphenoxy]phenyl) 2,2'-diphenyl-6,6'-biquinoxaline(IV). A rectangular bar sample that had been cured for one hour at 204°C, showed no sign of glass transition up to 350°C, in a dynamic mechanical measurement with the Rheometrics Mechanical Spectrometer at a scanning rate of 10°C/5 minutes. One could interpret such a result to mean the $Tg(n_i)$, where n_i is the cured state attained after one hour at 204°C is above 350°C. This is unlikely for obvious reasons. Probably this is the case where the kinetic rate is too fast, such that the only transition detectable is $Tg(\infty)$. $Tg(\infty)$ for this system is then above 350°C. This interpretation is supported by the DSC result. DSC scan of the sample of IV cured at 204°C for one hour showed further curing at temperatures above 200°C with no indication of a glass transition.

An alternative must be sought to detect $Tg(n)$ of both II and IV. The work on Epoxy 3501 has shown that $Tg(n)$ can be interpolated with TICA measurement (Reference 9). This Interpolation Technique used in that system is to construct the cure-phase diagram. Then with the two-step curing method, an isocured state curve can be superimposed on the cure-phase diagram. The combination of both data will then yield the $Tg(n)$ of the state of interest. The TICA technique is described in Reference 1. In this work, a slight modification of the sample preparation is implemented. A single layer of cloth was wetted with the solution of the resin to be studied. Solvent was subsequently removed with prolonged treatment under vacuum. Then the cloth was folded into quarter inch strips for mounting onto the sample plattens. TICA measurements of isothermal cure of IV however, indicated a very fast reaction rate. At 300°C, t_{Tg}, the time required to cure isothermally to the loss maximum, is comparable to the sample chamber heat-up time. This fact will make both the results from the two-step curing method and the cure-phase diagram unreliable.

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As shown from the epoxy work, we can prepare a series of samples with various known Tg. This is accomplished by isothermally curing a TICA sample and stopping the cure at the maximum of the vitrification peak. The specimen thus prepared would then have a Tg equal to the curing temperature. With this set of specimens, a calibration technique is developed to detect Tg(n).

Figure 2 is a typical response of an incompletely cured TICA specimen of IV post cured at 350°C. The frequency of measurement in all experiments in this report was 1.6 Hz (10 rad/sec). The sample chamber temperature was set at 0°C at the beginning. Then the digital dials indicating the desired control temperature were increased in steps of 10°C/5 sec. There will be a time lag between the convecting air temperature and the temperature indicated by the dials. Similarly a lag will exist between the air temperature and the specimen temperature. Therefore, the specimen temperature increase is not necessarily linear or well controlled, but it is highly reproducible. This reproducibility is critical in this experiment.

The softening of the specimen during the heat up is indicated by the decrease of the a component (Figure 2). The softening is due to the temperature effect on the specimen. The a component, after decreasing to a certain minimum, increases again which is due to the further curing of the specimen. The two effects are working against each other, so the amount of softening exhibited by the specimen is determined by its Tg value at the beginning of the experiment. That is why the temperature increase profile during heat-up being reproducible is an important factor in this experiment.

The amount of softening of the specimen during the 350°C post cure is dependent on the Tg(n) of the specimen. If the Tg(n) is above 350°C, there should be no softening, but if the Tg(n) is below 350°C, the amount of softening should decrease with increasing Tg(n). A parameter R is used to quantitize the amount of softening. R is defined as the ratio of β and ∞ in Figure 2.

$$R = \frac{\beta}{\infty}$$

The values of α and β are read off the post-cure behavior chart as the distances between the levels. The charts were plotted on the log scale, so in essence,

$$\alpha \propto \log \frac{G(0°C)}{G_x}$$

where $G(0°C)$ is the modulus of the partially cured specimen at $0°C$, G_x is the minimum modulus value during the heat up. Likewise,

$$\beta \propto \log \frac{G(350°C)}{G_x} \ ,$$

and

$$R = \frac{\log G(0°C) - \log G_x}{\log G(350°) - \log G_x}$$

with $G(350°)$ being the modulus value after curing at $350°C$.

The $\underline{R}$ values of IV at various Tg are listed in Table 1, and are plotted also in Figure 3. These results will serve as a calibration between $\underline{R}$ and Tg. A set of specimens cured at $200°C$ for various lengths of time were prepared. The $\underline{R}$ values were measured (included in Table 1). The R values are then translated to Tg's which are plotted vs time of cure in Figure 4. The results indicate that after the second hour of cure, the Tg stopped increasing and the maximum Tg was attained, as measured at 1.6 Hz (10/rad/sec), is 250 $\pm10°C$.

Similar experiments were performed on II and the results are listed in Table 2. Figure 5 is the calibration curve for II and Figure 6 is the Tg vs time of cure plot. The sample of II showed a faster kinetic rate than IV, with most of the curing occurring in the first hour. This is in agreement with the kinetic data obtained with DSC. The Tg however, was still increasing even after eight hours of cure, but at an extremely slow rate. After 16 hours, the specimen had a Tg of 280 $\pm10°C$, a higher Tg(n) value than IV.

TABLE 1

SOFTENING PARAMETERS ($\underline{R}$) FOR IV WITH VARIOUS CURE HISTORY

Temperature	R
229°C (Tg)	0.450
250°C (Tg)	0.401
300°C (Tg)	0.250
281°C (Tg)	0.286
267°C (Tg)	0.330
200°C/1 hr	0.526
200°C/2 hr	0.357
200°C/4 hr	0.388
200°C/6½ hr	0.375
200°C/14 hr	0.400

TABLE 2

SOFTENING PARAMETERS ($\underline{R}$) FOR II WITH VARIOUS CURE HISTORY

Temperature	R
297°C (Tg)	0.320
247°C (Tg)	0.432
198°C (Tg)	0.579
265°C (Tg)	0.400
200°C/1 hr	0.390
200°C/ 4 hr	0.370
200°C/ 14 hr	0.350

SECTION IV

EXPERIMENTAL

4-(3-Ethynylphenoxy)benzil was prepared by a reported procedure (Reference 6).

1. 2,2'-Bis(phenylethynyl)-5,5'-diaminobenzidine (I)

The preparation of this compound by a seven step procedure starting from 3-iodonitrobenzene has been previously reported (Reference 1). Some of the steps in this procedure were improved by the following synthetic modifications.

2. 3,3'-Diiodoazoxybenzene

A mixture of sodium hydroxide (172 g., 4.3 moles) and ethanol (500 ml.) was stirred and heated at reflux until most of the sodium hydroxide had dissolved. Ethylene glycol (600 ml.) was added, followed by 3-iodonitrobenzene (100 g., 0.402 mole). The reaction mixture was maintained at 100-110°C for two hours and poured into 4.1 of water. The precipitate was collected, washed thoroughly with water, and dried under suction to afford 76.0g. (85%) of crude 3,3'-diiodoazoxybenzene which was used without further purification for the following reaction.

3. N,N'-Diacetyl-2,2'-diiodobenzidine

To a solution of 3,3'-diiodoazoxybenzene (60.0 g., 0.133 mole) in 320 ml. tetrahydrofuran (THF) was added acetic acid (400 ml.), zinc dust (33.6 g., 0.513 mole), and 85% phosphoric acid (60 ml.). The reaction mixture was stirred for one hour at 23°C and then cooled to -5°C. Hydrochloric acid (120 ml.) was added at a rate such that the reaction temperature was maintained below 0°C. After completion of addition the reaction mixture was stirred for one hour at -5 -0°C followed by 90 minutes at 23°C, and then was poured into 1.1 of water. The aqueous solution was filtered, and the filtrate was made basic with 900 ml. of ammonium hydroxide and extracted with benzene (4x300 ml.). The combined benzene extracts were filtered through a bed of Celite, washed with water (2x600 ml.), and stirred for 16 hours with acetic anhydride (150 ml.). The white precipitate

of N,N'-diacetyl-2,2'-diiodobenzide was filtered, washed with benzene, and dried under vacuum at 60°C to afford 38.4g. (53%), m.p. 300-301°C.

4.   2,2'-Bis(phenylethynyl)-5,5'-dinitrobenzidine (III)

a. Reaction of 2,2'-diiodo-5,5'-dinitrobenzidene, phenylacetylene, bis-(triphenylphosphine) palladium dichloride, and cuprous iodide was carried out according to the procedure of Sonogashira, et. al. (Reference 7). It was found necessary to use a 1:1 mixture of diethylamine and dimethyl sulfoxide as the solvent for best results. Yields of III ranged from 12-31%.

b. Reaction of 2,2'-diiodo-5,5'-dinitrobenzidine, phenylacetylene, triphenylphosphine, and palladium (II) acetate in triethylamine was carried out according to the procedure of Dieck and Heck (Reference 8). TLC analysis (Bakerflex silica gel 1B-F/ether-benzene-hexane 1:1:1) indicated that all of the starting material had reacted, but no III was formed.

c. Preparation of III in 42-57% yield was successfully carried out by the previously reported procedure (Reference 1).

5.   2,2'-Bis(phenylethynyl)-5,5'-diaminobenzidine (I)

To a mixture of 2,2'-bis(phenylethynyl)-5,5'-dinitrobenzidine (4.70g., 0.00992 mole) and methanol (235 ml.) was added a solution of sodium dithionite (40.0g 0.23 mole) in water (140 ml.) and ammonium hydroxide (95 ml.). The reaction mixture was stirred and refluxed until TLC analysis (Bakerflex silica gel 1B-f/benzene) indicated complete absence of starting material (approx. 30-40 minutes). The appearance of the reaction during this period changed from a deep red-orange suspension to a light gray-tan suspension. The mixture was poured into 2500 ml. of water, stirred 15 minutes, and filtered. The filter cake was washed thoroughly with water and dried under suction for 15 minutes. The damp 2,2'-bis(phenylethynyl)-5,5'-diaminobenzidine, pure by TLC analysis (Bakerflex silica gel 1B-F/ethyl acetate), was used without further purification for the following reaction.

6.   3,3'-Bis(4-[3-ethynylphenoxy]phenyl)-7,7'-bis(phenylethynyl)-2,2'-
diphenyl-6,6'-biquinoxaline (II)

The 2,2'-bis(phenylethynyl)-5,5'-diaminobenzidine prepared as
described previously was dissolved in 150 ml. THF. This solution was
stirred under nitrogen while 4-(3-ethynylphenoxy) benzil (6.16g., 0.0189
mole) was added followed by acetic acid (2 ml.). The reaction mixture
was stirred at 23° for 16 hours and then precipitated into 750 ml. of
methanol to afford 5.40 g. of precipitate. Concentration of the filtrate
afforded an additional 1.01 g. for a total yield of 6.41 g. of II (65%
from 2,2'-bis[phenylethynyl]-5,5'-dinitrobenzidine).

Anal. Calcd, for $C_{72}H_{44}N_4O_2$: C, 86.72; H, 4.45; N, 5.62.   Found: C, 86.33
86.19; H, 4.54, 4.50; N, 5.57, 5.62.   NMR in $CDCl_3$ (PPM from TMS as internal
standard): 3.1, singlet, RI=1, (C≡C-H); 6.9-7.7, mult., RI=18 (aromatic C-H);
8.4, singlet, RI=1 (aromatic C-H); 8.5, singlet, RI=1 (aromatic C-H).

SECTION V

CONCLUSIONS

The Tg(n) results at 200°C of II and IV indicate that a system with IMC has better solid state curing capabilities than a system without, which underscores the feasibility of IMC as a means to improve curing of polymers. However, for this particular system, II, the advantage gained in Tg(n) vs IV is low under the cure conditions used. Perhaps the problem is that in this system, two types of curing reactions are occurring with similar kinetic dependence on temperature. The IMC reaction is not diffusion controlled, whereas the terminal acetylene curing reaction is. Because II reaches the vitrification point earlier, the terminal acetylene groups are less extensively reacted than the corresponding IV, thus compromising the advantage gained by IMC.

It must also be realized that, under the cure conditions used (200°C for two hours) neither the terminal acetylene sites nor the IMC acetylene sites are completely reacted. Fourier Transform Infrared studies of the reduction in intensity of the $(C \equiv C)-H$ stretch at 3295 cm-1 indicated 74% reaction for II and 88% reaction for IV. The IMC acetylene site was even less completely reacted; 59% as indicated by the $C \equiv C$ stretch at 2210 cm-1. It is thus possible that complete reaction of these sites by means of higher cure temperature and longer cure time might enhance the Tg differential between II and IV.

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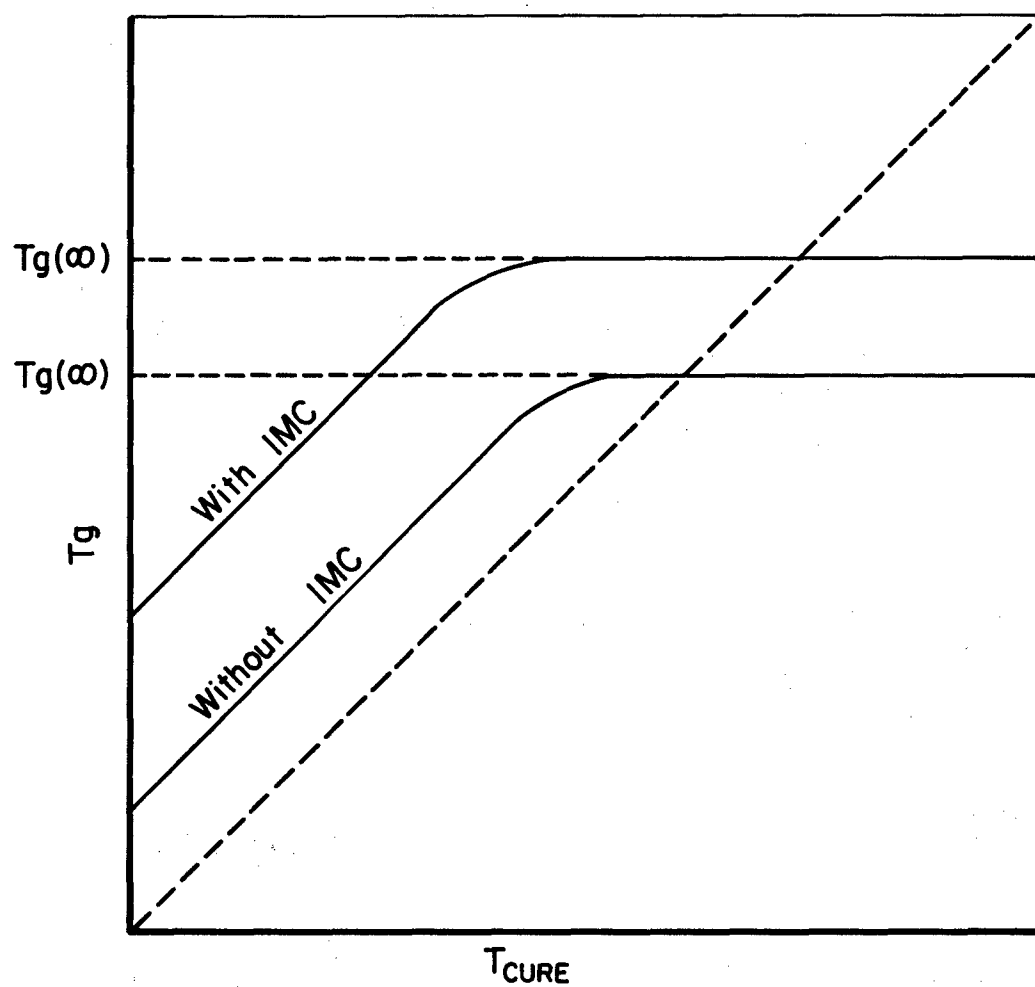
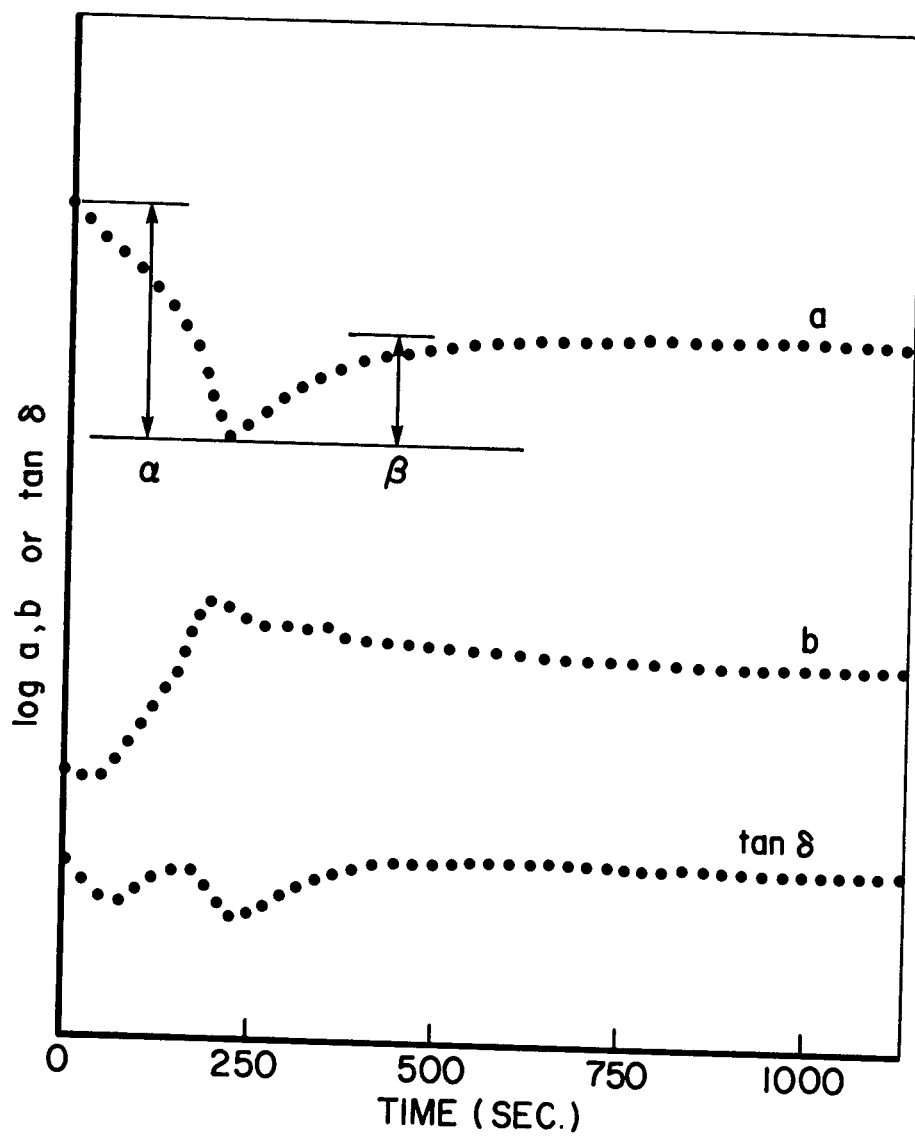Figure 1. Tg vs Cure Temperature Plot of Thermosetting Systems

Figure 2.   Post Cure Plot of a, b and tan δ of a TICA Sample Cured to
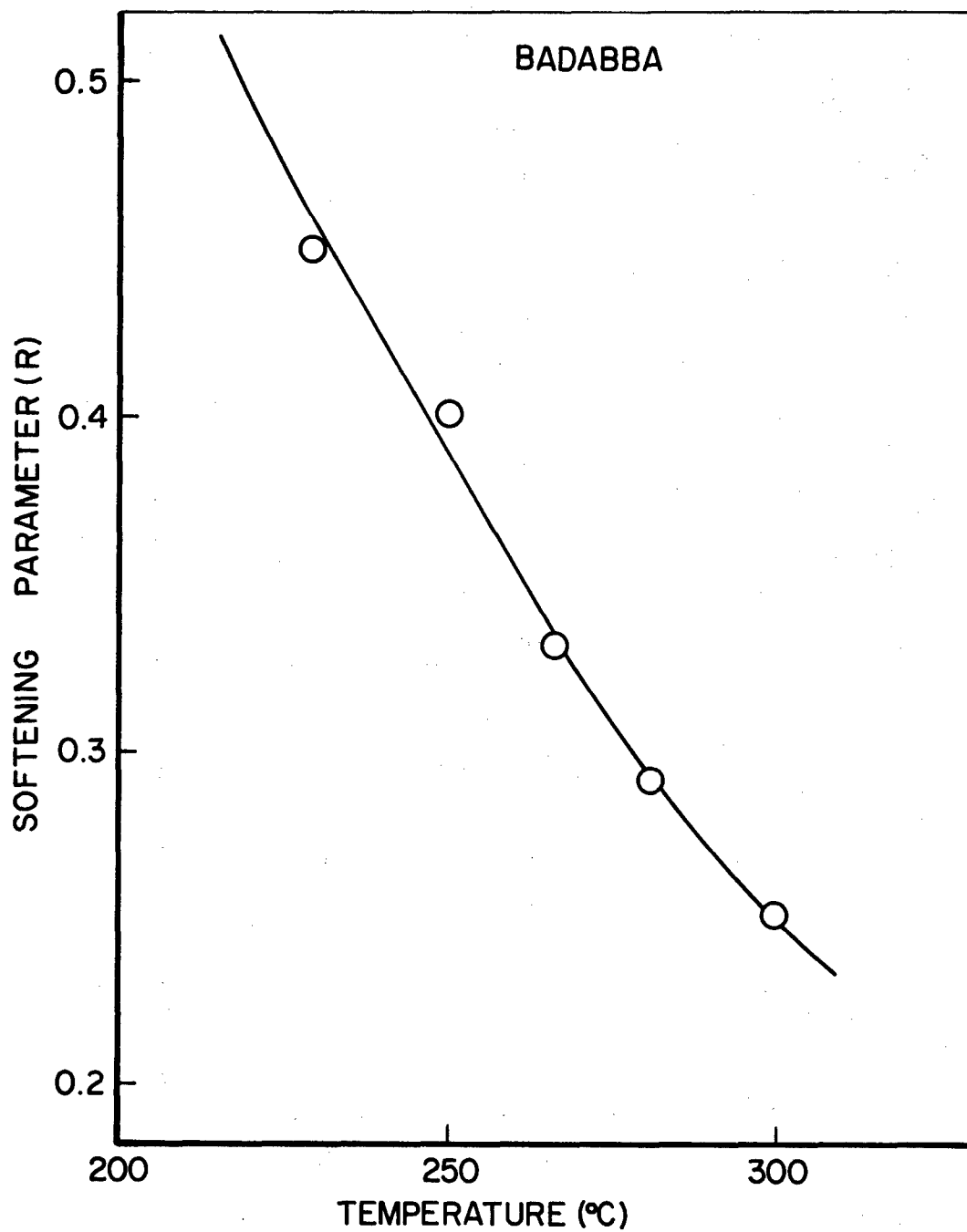b Maximum at 229°C

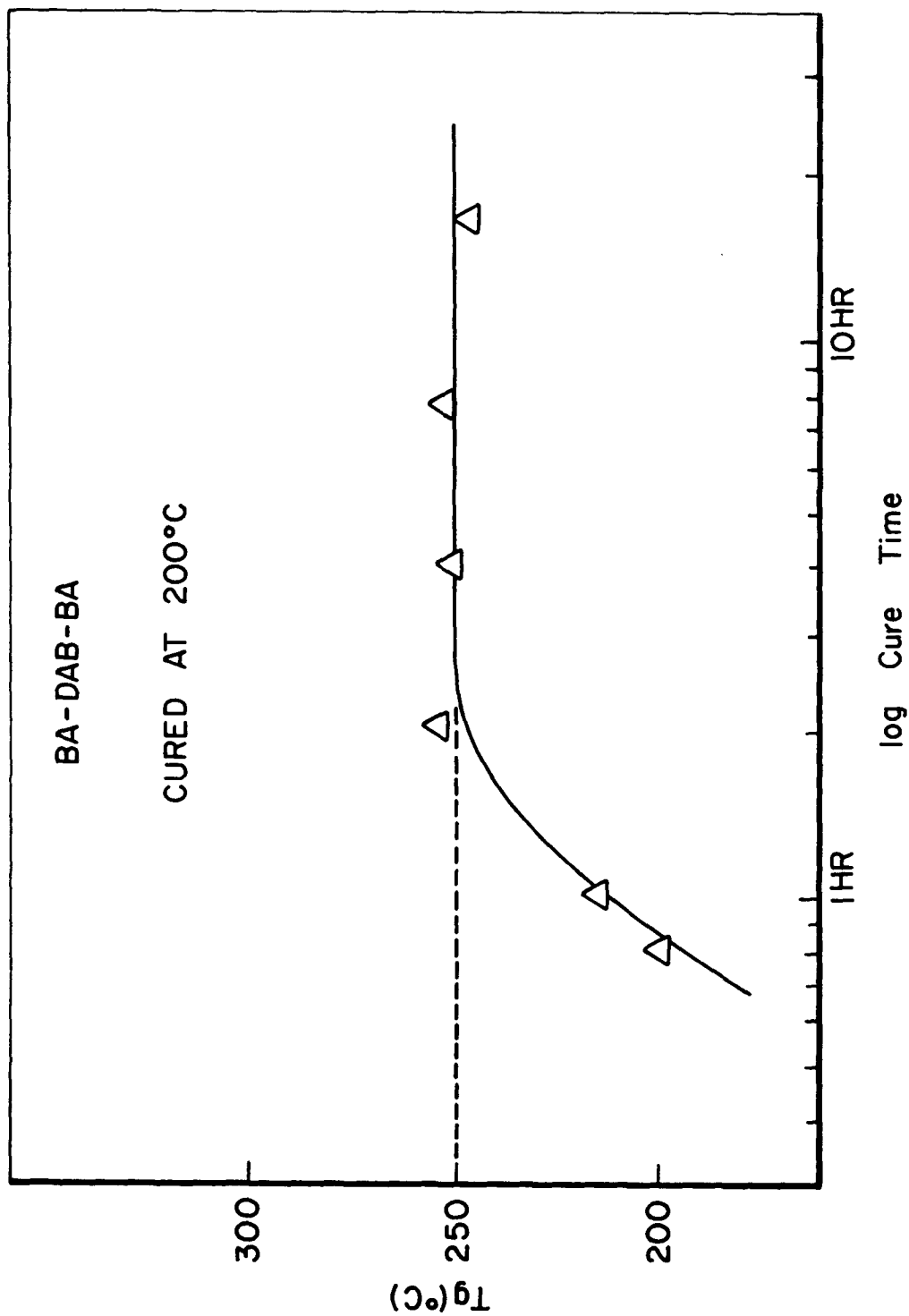Figure 3. Calibration Curve of R vs Tg for IV

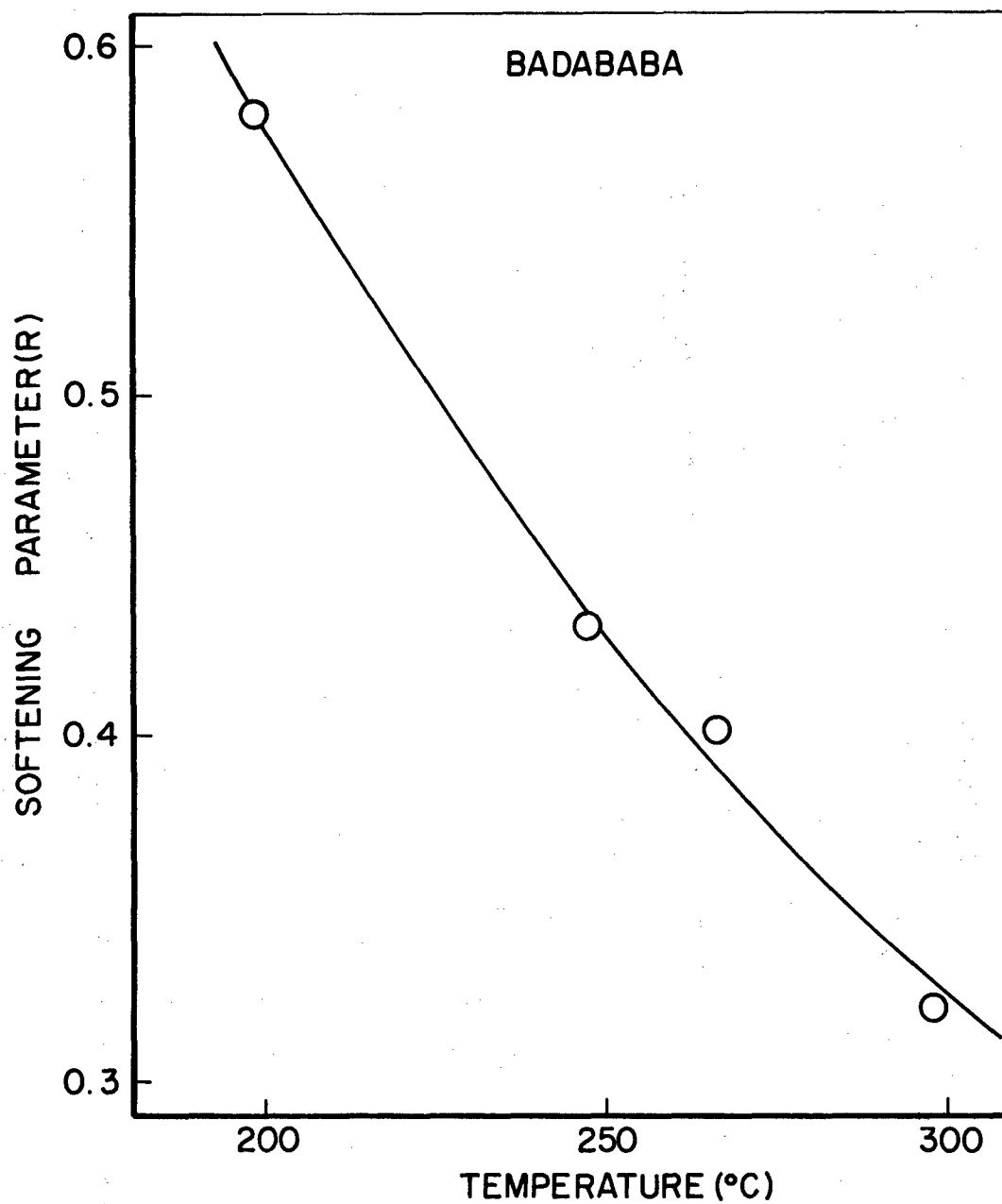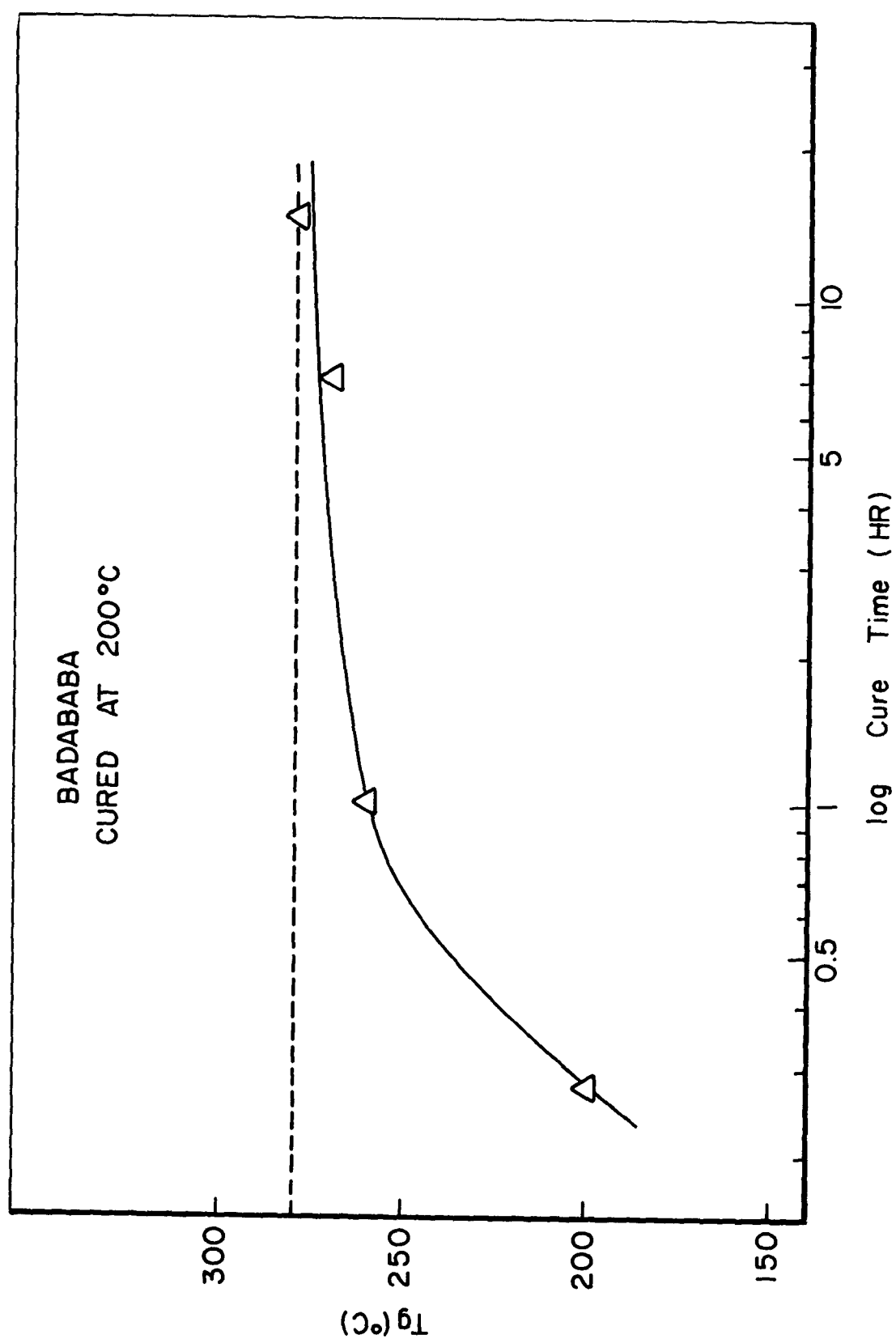Figure 4. Tg vs Cure Time Plot for IV

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Figure 5. Calibration Curve of R vs Tg for II

Figure 6.   Tg vs Cure Time Plot for II